A Numerical Evaluation of the Stochastic Completeness of the Kinetic Coagulation Equation

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ABSTRACT

The stochastic completeness of the kinetic coagulation equation depends on the extent of correlations between particle properties. Such correlations are induced by the coalescence process that causes spatial inhomogeneities in the number concentration of the particles, and are particularly strong in poorly mixed suspensions. A Monte Carlo simulation of the coalescence process is used to evaluate the suitability of the kinetic coagulation equation to simulate the coalescence process using Brownian diffusion, fluid shear and differential sedimentation collision kernels. It is demonstrated that the outcome of the kinetic equation matches well the true stochastic averages, unless the number concentration of particles involved is very small. In that case, the discrepancies between the two approaches are substantial in the large end of the particle size spectrum.

1. Introduction

The time evolution of $\hat{n}(i, t)$, the mean number of particles of size class i per unit volume, in a coagulating population of particles, is customarily described by

$$\frac{\partial \hat{n}(i, t)}{\partial t} = \frac{1}{2} \sum_{j=1}^{i-1} \beta(i-j, j)\hat{n}(i-j, t)\hat{n}(j, t) - \hat{n}(i, t) \sum_{j=1}^{\infty} \beta(i, j)\hat{n}(j, t), \quad (1)$$

where $\beta(i, j)$ is the probability that an arbitrary particle of size i will collide with an arbitrary particle of size j in unit time. This probability is also called the collision function and represents the geometry and dynamics of the collision mechanism. The two terms on the rhs of (1) represent, respectively, the rate of gain of particles of volume i by coagulation of pairs of smaller particles, conserving volume, and the loss of particles, i, due to their coagulation with particles of all sizes.

Equation (1) is a deterministic phenomenological equation and describes the behavior of the suspension averaged over some volume of fluid. More often than not, however, particles have a nonuniform spatial distribution and the collision process takes place in their actual location. In addition, correlations between the particles occur, induced by the coagulation process. For example, as particles of a given size in a region of fluid coagulate, a local reduction in their number occurs, so fewer particles of this size remain for further coalescence. Such spatial inhomogeneities, which can be expressed as conditional probabilities for the collision of two particles, are ignored in (1), which describes the mean behavior of the particles and is referred to in the literature as the kinetic equation of coagulation.

Since the collision process is nonlinear in particle number concentration, the average spectrum of the coagulating population of particles predicted by the kinetic equation may not represent the true average of the local coalescence processes. In fact, in the absence of the knowledge that the collision frequency is characterized by a single parameter, such as would be the case with a Poisson process, the use of a single-valued function $\hat{n}(i, t)$ to describe the number concentration of particles of size i at time t, is questionable. Instead, the time-evolution of the probability $P(n, i; t)$ must be computed, where $P(n, i; t)$ is the probability that n particles of size i will exist at time t in a unit volume of fluid. The first moment of $P(n, i; t)$ with respect to n will then give the mean number $\hat{n}(i, t)$ of particles of size i at time t per unit volume. Gillespie (1972) derived a time-evolution equation for $P(n, i; t)$ by considering all "mutually exclusive and collectively exhaustive ways" of realizing n i-sized particles at time $t + \Delta t$ and then taking the limit $\Delta t \to 0$. Defining the "conditional" probability $P(n, i|n', i'; t)$, that there are exactly n i-sized particles in the unit fluid volume at time t, given that there are already exactly n' i'-sized particles, and the "doubly conditional" probability $P(n, i|n', i'; n'', i''; t)$, that there are exactly n i-sized particles in the unit fluid volume at time t, given that there are already n' i'-sized particles and n'' i''-sized particles, Gillespie obtained the following equation:

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$$\frac{\partial P(n, i; t)}{\partial t} = \frac{1}{2} P(n-1, i; t) \sum_{\substack{i'=1 \\ i' \neq i/2}}^{i-1} \sum_{n'=1}^{\infty} \sum_{n''=1}^{\infty} n'n'' P(n', i'|n-1, i; t) \quad \times P(n'', i-i'|n-1, i; n', i'; t)\beta(i', i-i')$$

(a)

$$-\epsilon(i)\frac{1}{2} P(n-1, i; t) \sum_{n'=1}^{\infty} n'(n'-1) P\left(n', \frac{i}{2}\middle| n-1, i; t\right)\beta\left(\frac{i}{2}, \frac{i}{2}\right)$$

(b)

$$-\frac{1}{2} P(n, i; t) \sum_{\substack{i'=1 \\ i' \neq i/2}}^{i-1} \sum_{n'=1}^{\infty} \sum_{n''=1}^{\infty} n'n'' P(n', i'|n, i; t) \quad \times P(n'', i-i'|n, i; n', i'; t)\beta(i', i-i')$$

(c)

$$-\epsilon(i)\frac{1}{2} P(n, i; t) \sum_{n'=1}^{\infty} n'(n'-1) P\left(n', \frac{i}{2}\middle| n, i; t\right)\beta\left(\frac{i}{2}, \frac{i}{2}\right)$$

(d)

$$+(n+1)P(n+1, i; t) \sum_{\substack{i'=1 \\ i' \neq i}}^{\infty} \sum_{n'=1}^{\infty} n' P(n', i'|n+1, i; t)\beta(i, i')$$

(e)

$$-nP(n, i; t) \sum_{\substack{i'=1 \\ i' \neq i}}^{\infty} \sum_{n'=1}^{\infty} n' P(n', i'; |n, i; t)\beta(i, i')$$

(f)

$$+\frac{1}{2}(n+2)(n+1) \times P(n+2, i; t)\beta(i, i) - \frac{1}{2} n(n-1) \times P(n, i; t)\beta(i, i), \tag{2}$$

(g)

where

$$\epsilon(i) = \begin{cases} 1, & \text{if } i \text{ is even} \\ 0, & \text{if } i \text{ is odd.} \end{cases}$$

As a result of comparing the kinetic equation (1) with the stochastically complete equation (2), Gillespie concluded that the solution obtained from (1) will approach the true stochastic average provided: 1) that the probabilities of having n particles per unit volume of size i in the fluid at time t is independent of how many particles of various other sizes are present, and 2) that the coalescence of particles of equal size is prohibited. The first condition implies that

$$P(n, i|n', i'; t) \approx P(n, i; t), \quad \text{for} \quad i \neq i',$$

$$P(n, i|n', i'; n'', i''; t) \approx P(n, i; t), \quad \text{for} \quad i' \neq i \neq i'',$$

and, according to the second condition, the terms (b), (d) and (g) on the rhs of (2) vanish identically. In this case, Eq. (2) is reduced to the kinetic equation (1) by taking its first moment with respect to n.

The sensitivity of the kinetic equation to spatial fluctuations in particle concentration induced by the coalescence process has been extensively discussed in the literature. However, the complexity of the full stochastic coagulation equation necessitated the use of various assumptions in order to simplify the situation for mathematical treatment. Such assumptions (for example, the use of nonphysically derived collision functions) cast some doubt on the validity of comparisons between solutions to the kinetic equation and the true stochastic average spectrum.

In particular, the case of drops collecting droplets as they fall through a cloud has been the subject of several investigations in the attempt to explain the creation of raindrops in warm clouds. Gillespie (1975a), in an impressive contribution to coalescence studies, showed that all models for the growth of the drops employed at various times can be classified into three categories, depending on the physical in-

terpretation given to the quantity $A = \beta(M, m)n(m)dt$, where $n(m)$ is the number of droplets of size m:

1) The continuous model, according to which all large drops of mass M grow at the same rate collecting A number of droplets in time dt as they fall through a cloud with uniform water content;

2) The quasi-stochastic model, which is equivalent to solving the kinetic equation (1), and in which only a fraction A of the large drops with mass M collect a droplet in dt; and

3) The stochastic model, according to which fluctuations are permitted in the number of droplets collected by any drop, so that A represents the probability that any drop of mass M will collect a droplet of mass m in dt.

Telford (1955) showed that, under the assumption of constant number concentration of droplets, the growth rate of the large drop is faster in the quasi-stochastic than in the continuous model. Berry (1967), using a collision function proportional to the sum of the masses of the drop and the droplet, found that the growth rate predicted by the kinetic equation is twice that predicted by the continuous model; the difference in the growth rates predicted by the two models was negligible when a collision function proportional to the difference in the masses was used. A Monte Carlo technique was used by Chin and Neiburger (1972) to simulate the random positioning of droplets. Assuming that the initial droplet spectrum is time-invariant, they found that the size of the large drop computed with the kinetic equation model was significantly larger than the ensemble average drop size predicted by the Monte Carlo calculations. Their numerical solution of the kinetic equation gave a spectrum more "diffuse" than the Monte Carlo simulation. Various authors (Warshaw, 1967; Long, 1971; Twomey, 1966) discussed the consequence of poorly mixed clouds and asserted that fluctuations in the water concentration will result in the production of raindrops much faster than in a cloud with uniform water content.

Bayewitz *et al.* (1974) obtained an exact solution of the full stochastic equation for the case of a constant collision function. Their results suggest that for small populations of particles, the size spectrum predicted by the kinetic equation may differ significantly from the true stochastic average spectrum, particularly in the long tail of the distribution. In addition, Bayewitz *et al.* reason that the differences would be enhanced if a size-dependent collision function is used, since in that case, particle correlations would be stronger.

Finally, Gillespie (1975b) outlined a rigorous Monte Carlo simulation of the stochastic coalescence process, which avoids all assumptions included in the kinetic equation (1), but did not apply this technique to actual collision functions.

The numerous theoretical analyses and computational techniques employed so far seem not to have resolved the questions with regard to the suitability of the kinetic equation in describing the physics of the collision and coalescence processes in a poorly mixed suspension of particles. In their comprehensive review of the current state-of-the-art in coalescence modeling, Pruppacher and Klett (1978) emphasize the necessity of reexamining the reliability of the kinetic equation as applied to coalescence studies. Because coagulation occurs on scales extending from the microcosm of Brownian particle motion to the astronomical length scales associated with movement of galaxies over millions of years (Hockney and Eastwood, 1981), it is of interest to resolve this question. In this paper we attempt to address the stochastic completeness of the kinetic equation by a direct comparison of numerical solutions to the kinetic Eq. (1) with solutions to the stochastically complete Eq. (2) using Gillespie's (1975b) Monte Carlo method.

2. Numerical techniques

Numerical integration of the set of the coupled differential Eqs. (1) was performed using Gear's (1971) modification of Adam's multistep variable-order predictor–corrector method. Gear's method uses information from the previous steps to predict the derivative functions and extrapolate them into the next interval, therefore allowing a progressively larger step size. The use of (1), as opposed to methods that divide the particle size (radius or mass) range into size sections, within which a property of the particles remains constant (as, for example, the technique developed by Gelbard *et al.*, 1980), severely restricts the number of particle sizes that can be considered, because of computational cost. However, for the purposes of this work this is not a limitation; moreover, (1) provides the resolution in particle size space required to detect the possibly small differences between the two numerical approaches.

The Monte Carlo simulation technique (see Gillespie, 1975b, for details) uses the particle size spectrum at time t to construct the size spectrum at time $t + \Delta t$ by generating a random triplet $(\Delta t, i, j)$, distributed according to the joint probability density function for the occurrence of a coalescence between particles with sizes i and j during the time step Δt. The ensemble average of many successive realizations (i.e., computer runs) starting with the same initial particle size distribution gives then the true stochastic average spectrum at any desired time t. Gillespie's method is easily modified to include a spatial sink of particles, such as the removal by settling of particles from the fluid volume. If $N_k(i, t)$ represents the number of particles of size i at time t in run k in the fluid volume, then the change of the number of i-sized particles by settling during the time step Δt is described by

$$N_k(i, t + \Delta t) = N_k(i, t) \exp [-w_s(i)\Delta t/h],$$

where $N_k(i, t + \Delta t)$ is the number of i-sized particles in the fluid volume in run k at time $t + \Delta t$, $w_s(i)$ is their Stokes's settling velocity and h is the vertical dimension of the fluid volume. Note, however, that this formulation, although compatible with the addition of the term $-\hat{n}(i, t)w_s(i)/h$ on the rhs of (1), ignores the spatial inhomogeneities of the particles within the fluid volume induced by the settling process. The use of the settling term is convenient in order to overcome the problem of numerical loss of mass due to production by coalescence of particles larger than the largest size section considered in the simulations: settling removes particles from the largest size section faster than they are created by coagulation. In addition, this scheme allows a comparison of the reduction of the total volume concentration (defined as the volume of all particles averaged over the fluid volume) with time, as predicted by the kinetic equation and the Monte Carlo method and, consequently, a comparative evaluation of the two approaches at different volumetric concentrations. Pearson *et al.* (1984), using a Monte Carlo simulation of the coagulation process, showed that the removal of a few large particles by sedimentation does not disturb the coagulation kinetics of the particles in the smaller size ranges. Similarly, the breakup of large particles, which is not included here, is not expected to influence the comparative evaluation of the kinetic and Monte Carlo techniques in handling specific collision kernels.

For particles to coagulate, two processes are required: 1) a mechanism to develop relative motion of the particles through the fluid, which will bring them into close proximity, and 2) short-range interfacial forces acting between the particles to bring about their coalescence. Relative motion of particles in a fluid can be due to one or a combination of Brownian or thermal motion of the particles, laminar or turbulent fluid shear or straining, particle inertia in turbulent flows and differential sedimentation of particles of unlike sizes. For simplicity, interparticle forces are ignored here so that particles coalesce upon collision. In this case, relatively simple analytic estimates for the collision probability β (collision function or collision kernel) are available and are summarized in Table 1. The table also includes the dimensional parameters that characterize the mechanism and determine, in any given situation, the characteristic size of particle that they affect. Since the functional dependence of β on the sizes of the interacting particles is of importance to this work, only three cases need to be considered; namely, Brownian motion, laminar shear and differential sedimentation-induced coagulation. Inclusion of interparticle forces could be an extension of this work using the collision efficiencies developed by Valioulis and List (1984).

The evolution of the size distribution of a coagulating population of particles subjected to one of the three aforementioned mechanisms is followed by both the kinetic equation and the Monte Carlo method. The predicted size distributions are then compared at various times in the presence or absence of particle removal by settling. Particle size distributions obtained usually extend over two decades in particle volume. In both numerical schemes, all lengths are expressed as multiples of the radius of the smallest initial particle r_0. Particle volumes are described as multiples of the initial particle volume v_0. Time steps are specified as multiples of a characteristic time defined by the time scale necessary to nondimensionalize the equations for the appropriate colli-

TABLE 1. Collision functions and characteristic dimensional parameters for various particle collision mechanisms. Values of $\beta[L^3T^{-1}]$ are for collision mechanisms acting individually with no hydrodynamic or other interparticle forces.*

Mechanism	Collision function β	Source	Dimensional parameter
Brownian motion	$\frac{2kT}{3\nu}\frac{(r_i + r_j)^2}{r_i r_j} = 4\pi(D_i + D_j)(r_i + r_j)$	Smoluchowski (1916)	$K_b = \frac{kT}{\mu}\ [L^3T^{-1}]$
Laminar shear	$3.33G(r_i + r_j)^3$	Smoluchowski (1917)	$G[T^{-1}]$
Pure srain (extension)	$4.89\dot{\gamma}(r_i + r_j)^3$	Zeichner and Schowalter (1977)	$\dot{\gamma}[T^{-1}]$
Isotropic turbulent shear	$1.3\ (r_i + r_j)^3(\epsilon/\nu)^{1/2}$	Saffman and Turner (1956)	$\left(\frac{\epsilon}{\nu}\right)^{1/2}[T^{-1}]$
Turbulent inertia	$\frac{1.27(\rho_p - \rho_f)}{\mu}\left(\frac{\epsilon}{\nu}\right)^{1/4}(r_i + r_j)^2\lvert r_i^2 - r_j^2\rvert$	Saffman and Turner (1956)	$\frac{(\rho_p - \rho_f)}{\mu}\left(\frac{\epsilon}{\nu}\right)^{1/4}[LT^{-2}]$
Differential sedimentation	$\frac{0.7g(\rho_p - \rho_f)}{\mu}(r_i + r_j)^2\lvert r_i^2 - r_j^2\rvert$	Findheisen (1939)	$K_{ds} = \frac{g(\rho_p - \rho_f)}{\mu}\ [L^{-1}T^{-1}]$

* *Notation:* k: Boltzmann constant, T: absolute temperature, r_i: particle radius, μ: coefficient of fluid viscosity, D_i: particle diffusivity, G: laminar shear rate, $\dot{\gamma}$: extension rate, ϵ: viscous dissipation rate per unit mass, ν: kinematic viscosity of fluid ($=\mu/\rho_f$), ρ_f: fluid density, ρ_p: particle density, g: acceleration of gravity.

sion function. Particle size distributions are defined as a relative fraction of the initial particle number concentration found in any size range i, i.e., the size distribution is specified by the fraction n/n_0 where n_0 is the initial number per unit volume of the elemental particle.

Using this scheme of normalization it is relatively easy to show that the appropriate collision time scale for each coagulation is as follows:

$$\text{Brownian diffusion } t_b = [n_0 r_0 D_0]^{-1},$$

$$\text{Shearing motion } t_s = (n_0 r_0^3 G)^{-1},$$

$$\text{Differential sedimentation } t_d = \mu[n_0 r_0^4 g(\rho_p - \rho_f)]^{-1}.$$

Whereas, for settling of particles the time scale is

$$t_f = \mu h[r_0^2 g(\rho_p - \rho_f)]^{-1}.$$

In the above, D_0 is the molecular diffusivity of an elemental particle of radius r_0, which is initially present in concentration (number/unit volume) n_0; G is the rate of shearing strain, μ the fluid viscosity, ρ_p the particle density and ρ_f the fluid density. The settling time scale t_f is effectively the time required for an elemental particle to fall through a height h, the vertical dimension of the physical configuration. The collision time scale is roughly the expected time between collisions of elemental particles at the initial concentration n_0. Alternatively, the reciprocal of this time scale can be thought of as the average collision-frequency. Thus, if the ratio of t_b/t_f is large, we expect few Brownian motion-induced particle collisions of elemental particles in the time a particle falls through a height h.

In Brownian motion the thermal impact of molecules causes suspended particles to perform random motions relative to the bulk fluid. The diffusivity D_i of an i-sized particle, that is, of a particle consisting of i elemental particles, can be obtained in terms of the diffusivity D_0 of an elemental particle by

$$D_i = D_0 \times i^{-1/3},$$

where $D_0 = kT/(6\pi\mu r_0)$, k is Boltzmann's constant and T is the absolute temperature. Typically an initially mono- or polydisperse distribution of 100 to 200 particles per unit volume is assumed with a volume concentration c_0 of 1–3%. A high volume concentration and a limited particle size range are necessary in order to minimize computational costs and obtain results within reasonable times. The small number of particles necessitates ensemble averaging over a large number of runs, typically 1000, but reduces the storage requirements of the simulations. In addition, any differences in the results obtained by the two approaches are amplified when the number concentration of particles involved is small. For example, preliminary simulations showed that the size distributions predicted by the two models starting with an initial number of morer than 200 particles per unit volume were identical until the number of particles in the fluid volume was reduced by coalescence to less than ~100. The fact that both solutions were identical is, in itself, a good check on the coding and numerical calculations.

In the analysis, an initially mono-disperse system of 100 particles in a unit volume, with a volume concentration of 1.13%, is subjected to Brownian

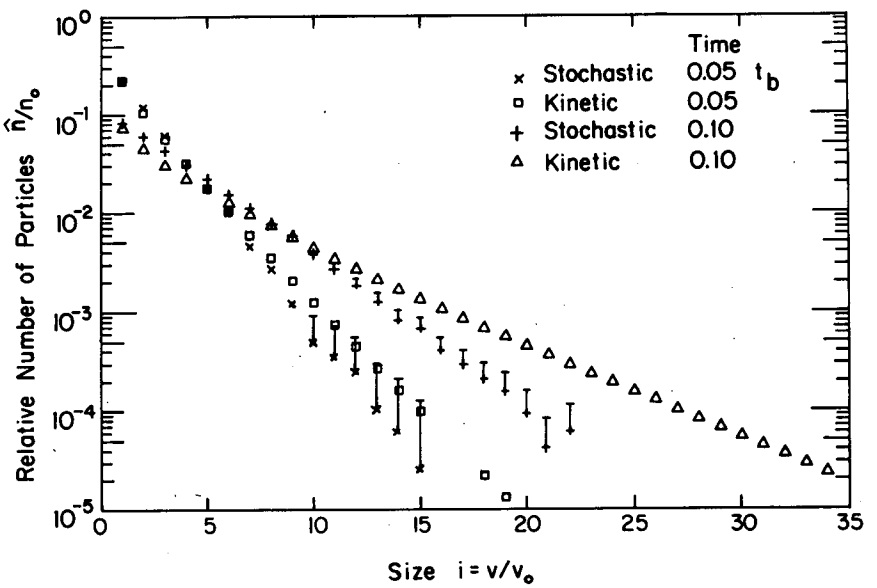

FIG. 1. Average particle size spectrum in Brownian diffusion. The vertical lines give the upper bound of the 95% confidence interval. Time scale $t_b = (n_0 r_0 D_0)^{-1}$, $c_0 = 1.13\%$.

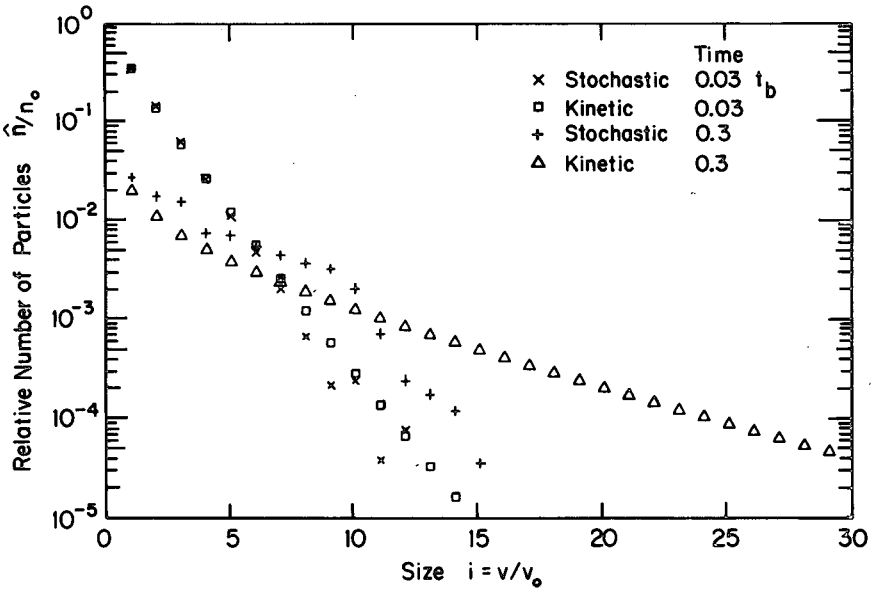

FIG. 2. Average particle size spectra in Brownian diffusion in the presence of particle removal by settling. Time scale $t_b = (n_0 r_0 D_0)^{-1}$, $t_b/t_f = 6$, $c_0 = 2.26\%$.

diffusion; its evolution is followed using both the kinetic equation (1) and the Monte Carlo technique. Time is nondimensionalized with the time scale t_b. Coagulation transfers mass toward large particle sizes, and the distribution spreads as time progresses. The mean particle size distributions computed with both models at two different times are plotted in Fig. 1 as a function of relative particle volume v/v_0, with v_0 the volume of an elemental particle. The relative number distributions $\hat{n}/n_0$ obtained must be interpreted as the "expected" ones that include all histories of particle growth as traced by the two models. The data points predicted by the Monte Carlo method are averages over 1000 runs. Even with this averaging there is still some statistical scatter in the data, especially at the lower end of the size distribution where very small numbers of particles are actually involved. The upper bound of the 95% confidence interval ($\sim +2\sigma$, where σ denotes the standard deviation), assuming a Gaussian distribution of the number of particles of a given size in the fluid volume, is drawn in the same figure, in order to evaluate statistically the differences in the results obtained (the lower bound of the 95% confidence interval is close to zero). The size distribution predicted by the kinetic equation differs from the true stochastic average spectrum, the difference becoming statistically significant as the time advances and the relative number concentration of suspended particles is reduced. With an initial number density of 100 particles per unit volume, the Monte Carlo technique produces an average number of 46.9 and 34.4 particles per unit volume at times $0.05t_b$ and $0.1t_b$, respectively; the corresponding figures for the kinetic model are 45.8 and 24.9. The relative size of the average particle in the size distribution predicted by the Monte Carlo calculations at these two times is 2.9 ± 0.12 and 21.4 ± 0.54 respectively. That is, at $0.1t_b$ the average particle consists of 21.4 elemental particles with a standard deviation $\sigma = 0.27$.[2] The values are, respectively, 4.0 and 21.8 in the kinetic equation result. The kinetic model predicts a more "diffuse" size distribution with a small number of very large particles in the fluid volume but with fewer particles overall.

For Brownian motion in the presence of particle removal by settling, the additional time scale t_f is introduced to characterize the settling of the particles as previously discussed. With a ratio $t_b/t_f = 6$, the size distribution evolution predicted by the two models is similar when an initially monodisperse population of elemental particles at an initial volume concentration of 2.26% is allowed to evolve in the presence of settling (Fig. 2). However, the relative volume concentration of particles is reduced as the coalescence proceeds and the larger particles are removed by settling, as shown in Fig. 3. At any given instant, more mass is predicted to be lost from the fluid volume according to the kinetic model. This is a

[2] The average size of the particles in each run is a member of a sequence of identically distributed random variables generated by a large number of independent realizations of the coalescence process. Thus, it can be justifiably argued that this sequence possesses the central limit property and estimate confidence intervals, assuming that the sample mean is approximately normally distributed.

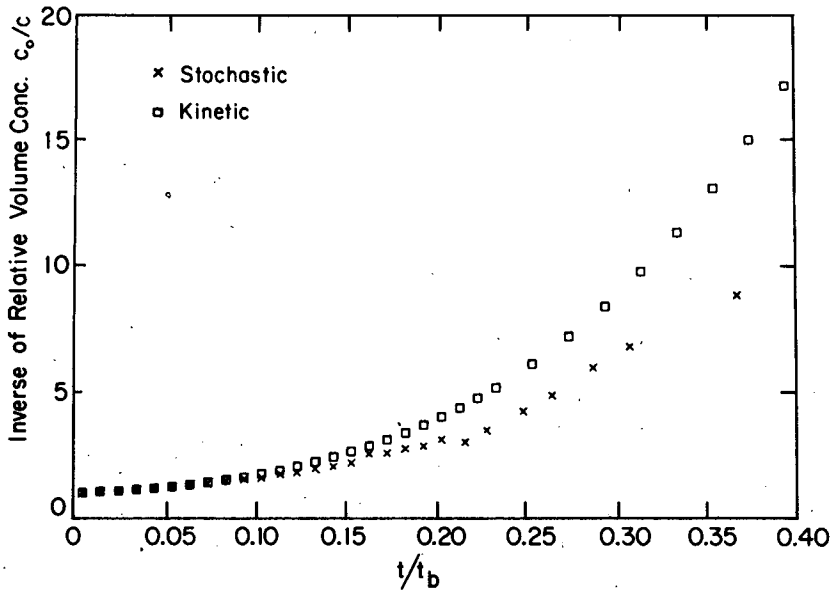

FIG. 3. Evolution of the particle volumetric concentration in Brownian diffusion. Time scale $t_b = (n_0 r_0 D_0)^{-1}$, $t_b/t_f = 6$, $c_0 = 2.26\%$.

direct consequence of the higher number density of large particles the kinetic model predicts at any time, as shown in Fig. 2.

When a uniform velocity gradient is imposed on an initially monodisperse population of 100 elemental particles at an initial volume concentration of 1.13%, the shear strain is the predominant collision mechanism. In this case, the time scale in the simulation is t_s. The results of both numerical techniques are indistinguishable for most of the size spectrum except near the large relative sizes, as is seen in Fig. 4. Because of the limited particle size range that could be followed in the simulations, the evolution of the particle size distribution could not be computed for later times, since large particles, larger than the largest size included in the simulations, would have been created. In order to overcome this difficulty and to determine whether the size distributions predicted by the two models in shear induced coagulation are statistically similar at smaller number concentrations,

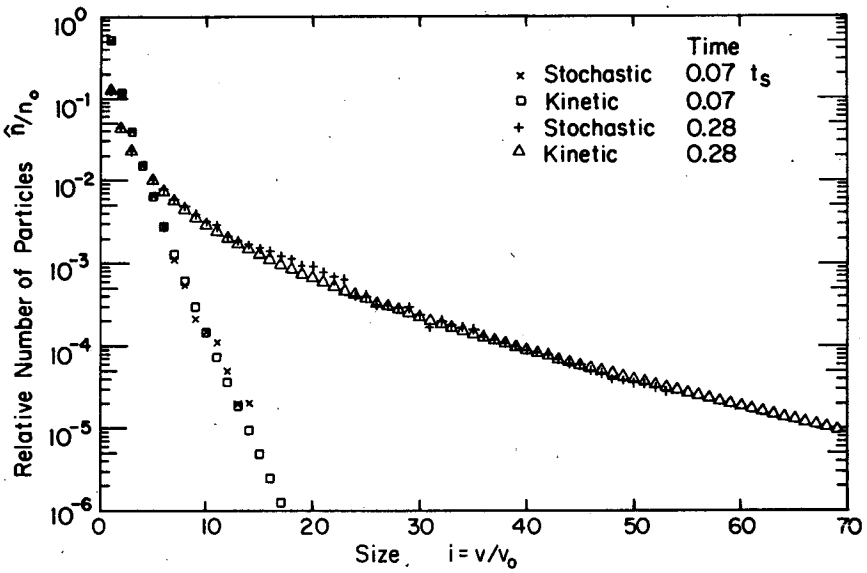

FIG. 4. Average relative size spectra in laminar shear. Time scale $t_s = (n_0 G r_0^3)^{-1}$, $c_0 = 1.13\%$.

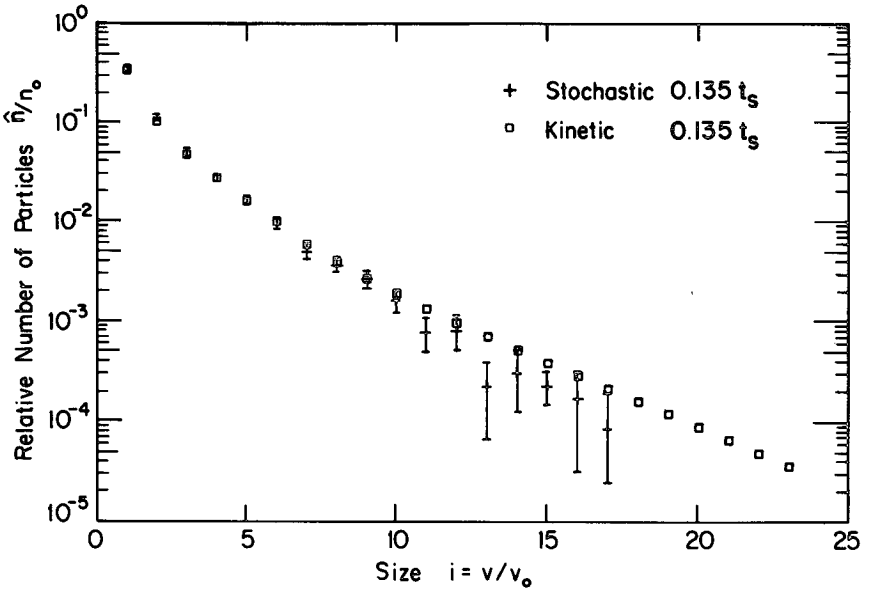

FIG. 5. Average particle size spectra in laminar shear at time $0.135t_s$. Time scale $t_s = (n_0 r_0^3 G)^{-1}$, $c_0 = 1.13\%$.

the number concentration of the particles in the initial monodisperse population was reduced to 40, at the same volumetric concentration, and the simulations repeated. The size distributions generated at times $0.135t_s$ and $0.34t_s$ are shown in Figs. 5 and 6, respectively, along with the 95% confidence intervals. The size distributions are statistically identical over most of the size range but the kinetic model predicts a finite number of large particles, while, for example, the probabilistic model produces no particles larger than $18v_0$ at $0.135t_s$ and none larger than $30v_0$ at $0.34t_s$. The average size and number of the particles at $0.34t_s$ is 4.67 and 8.02, respectively, according to the kinetic equation, and 3.62 ± 0.20 and 10.98 ± 0.30 according to the Monte Carlo calculations. The probabilistic approach predicts a particle population greater in number but with a smaller mean size. The numerical results presented in Figs. 4, 5

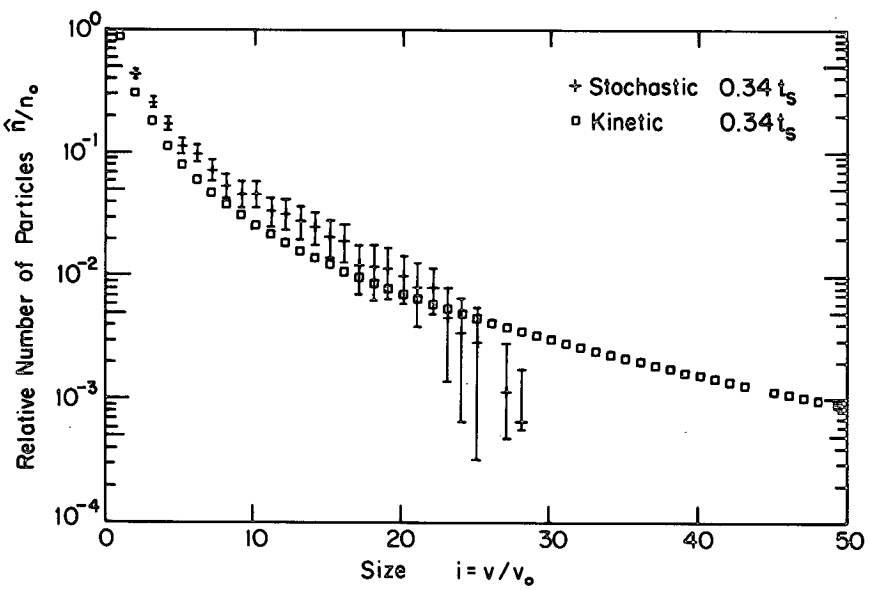

FIG. 6. As in Fig. 5 but for time $0.35t_s$.

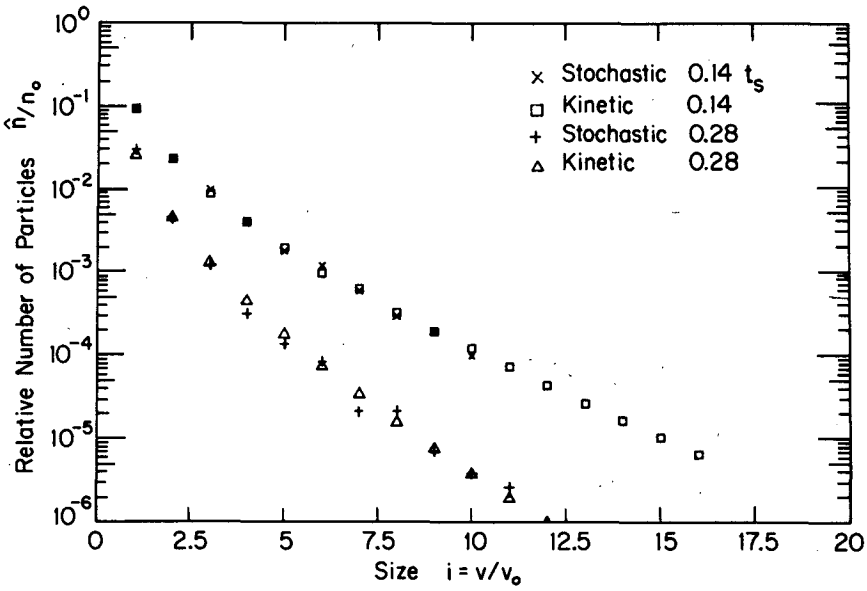

FIG. 7. Average particle size spectra in laminar shear in the presence of particle removal by settling. Time scale $t_s = (n_0 r_0^3 G)^{-1}$, $t_s/t_f = 16$, $c_0 = 2.26\%$.

and 6 are in agreement with the implication of the nondimensionalization of the kinetic coagulation equations, namely, that the relative number of particles $\hat{n}/n_0$, of any specified relative size v/v_0, is a function of t/t_s and independent of the absolute initial particle number concentration. However, these results graphically show that the same conclusion is not true for the solutions obtained from the exact stochastic definition of the problem. Clearly, when the initial number concentration of particles is low, then the joint probabilities assumption made in the derivation of (1) from (2) begins to become an important factor.

When a monodisperse system of 200 elemental particles is subjected to shear induced coalescence and simultaneous removal by settling, the predictions of both models are identical, both with regard to the evolving size distributions (Fig. 7) and the volumetric concentration of the particles (Fig. 8), even when the

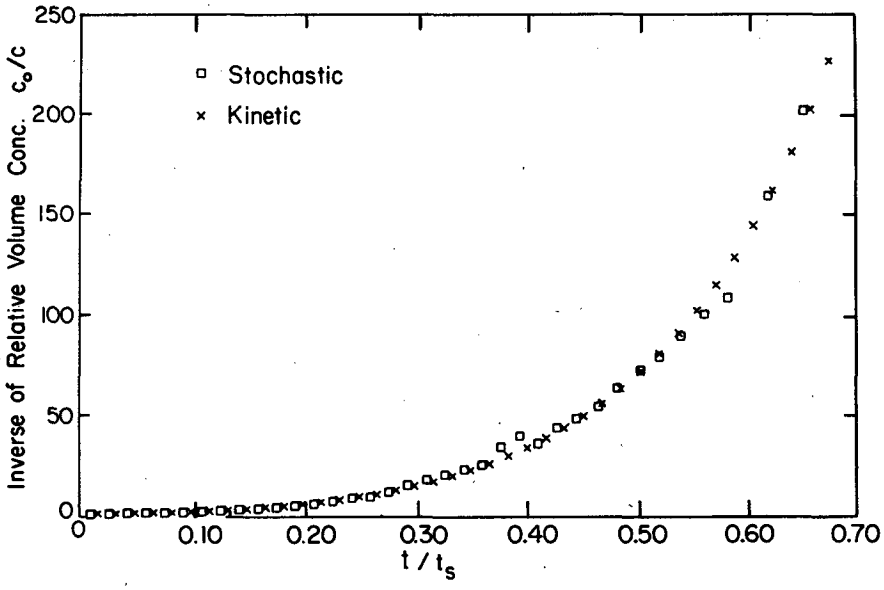

FIG. 8. Evolution of the particle volumetric concentration in laminar shear. Times scale $t_s = (n_0 r_0^3 G)^{-1}$, $t_s/t_f = 16$, $n_0 = 200$, $c_0 = 2.26\%$.

number of particles left in the fluid volume corresponds to a volume concentration as low as 1/400 of the initial. The large t_s/t_f ratio of these simulations indicates that the suspension is well-mixed so that coalescence-induced correlations between the particles are unimportant.

As discussed in the Introduction, the growth of a single particle as it falls through smaller ones has been the subject of several investigations with controversial results. Here we let a single particle, whose volume is twice any of the rest, settle through a monodisperse suspension of 200 particles in a unit volume at a volumetric concentration of 2.34%. We then follow the growth of this large particle with the two models and compute the probability $P(i, t)$ of the large particle having volume i at time t. The time is nondimensionalized with the differential time scale t_d. The probability distributions obtained at three different times are shown in Fig. 9. The data points shown are averages over 1000 independent realizations of the growth of the large particle and are normalized with its mean size $\bar{v}$ at that time, so that the area under the curve defined by the data points is unity. At times $0.15t_d$ and $0.30t_d$ the results collapse on the same curve, but they differ slightly at $0.45t_d$. The size of the average large particle in the Monte Carlo simulation is 11.9 ± 0.16, 18.75 ± 0.60 and 30.78 ± 0.83 (with 95% confidence) at the times $0.15t_d$, $0.30t_d$ and $0.45t_d$, respectively, while the kinetic equation gives 12.01, 18.96 and 30.95. Thus, the two models predict a statistically similar growth rate for the large particle. In order to evaluate the influence of the number concentration of the small particles on the probability density function $P(i, t)$ of the size of the large particles, we repeated the calculations starting with an initial number of 20 particles, 19 of them being elemental and 1 having the volume of two elemental particles. The volumetric concentration of the particles is 0.45%. The $P(i, t)$ at times $0.1t_d$ and $0.5t_d$ as predicted by the two models is shown in Figs. 10 and 11, respectively, along with the 95% confidence intervals. Contrary to the case presented in Fig. 9, the Monte Carlo technique predicts a faster growth for the average size of the large particle: at times $0.1t_d$ and $0.5t_d$ the average size is 9.63 and 11.7, respectively, according to the kinetic model, while the Monte Carlo method gives 10.03 ± 0.08 and 12.38 ± 0.12 (at 95% confidence), a statistically significant difference. In addition, the probability density functions for the size of the large particle have a strikingly dissimilar shape at time $0.5t_d$. Although the kinetic equation predicts a slower growth rate for the average size, it gives a higher probability for the occurrence of large particles. This result is of significance in atmospheric sciences, since rain formation in warm clouds is very sensitive to the growth rate of large particles.

Differential sedimentation-induced coagulation in the presence of particle removal by settling is treated identically by the two models. Witness the next two figures which present the evolving particle size distributions at four different times (Fig. 12) and the time dependence of the total volumetric concentration (Fig. 13).

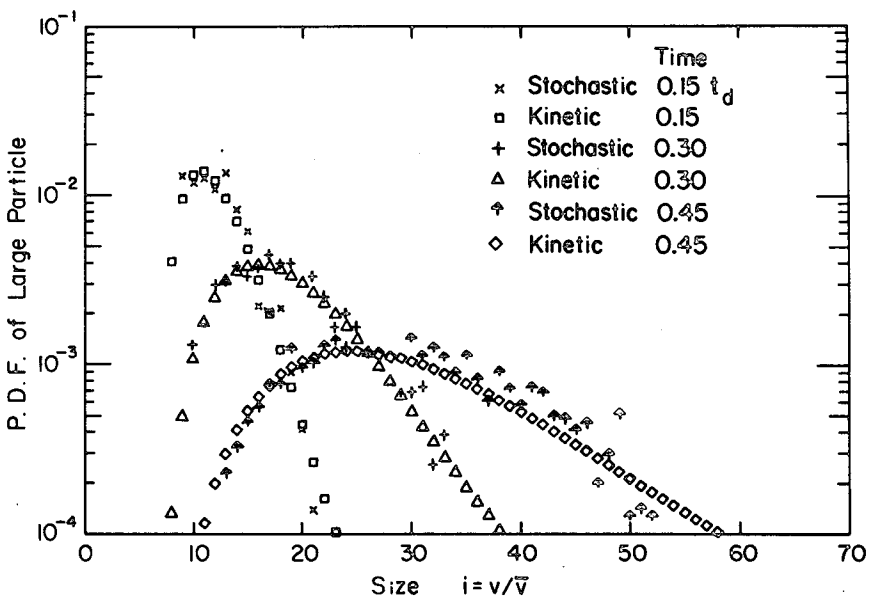

FIG. 9. Probability density functions of the growth of a large particle settling through a monodisperse population of 199 elemental particles. Time scale $t_d = \mu/[n_0 r_0^4 g(\rho_p - \rho_f)]$, $c_0 = 2.26\%$.

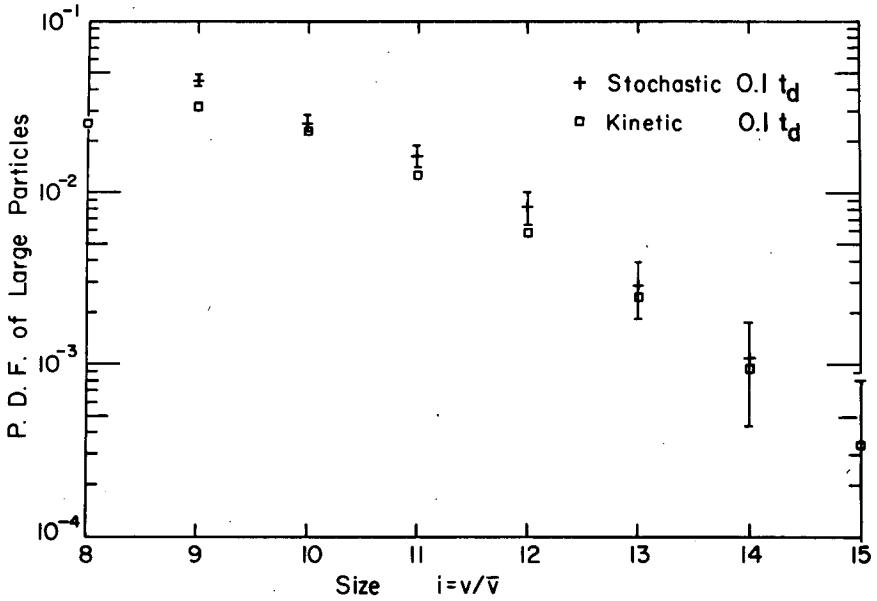

FIG. 10. Probability density functions at time $0.1t_d$ of the growth of a large particle settling through a monodisperse population of 19 elemental particles. Time scale $t_d = \mu/[n_0 r_0^4 g(\rho_p - \rho_f)]$, $c_0 = 0.45\%$.

3. Discussion and conclusions

The main aim of this study was to examine the stochastic completeness of the kinetic coagulation equation (1) as applied to coalescence studies. At issue is the adequacy of the kinetic equation to represent the coagulation process in poorly mixed suspensions. In such particle systems, coalescence proceeds locally under the conservation of particle mass constraint, so that, inevitably, a small population of particles occurs at some point in time. This is precisely the situation in which particle correlations are apt to occur, induced by the spatial inhomogeneities in the number concentration of particles created by the coalescence process. Although the number of particles in any physical system is usually very large,

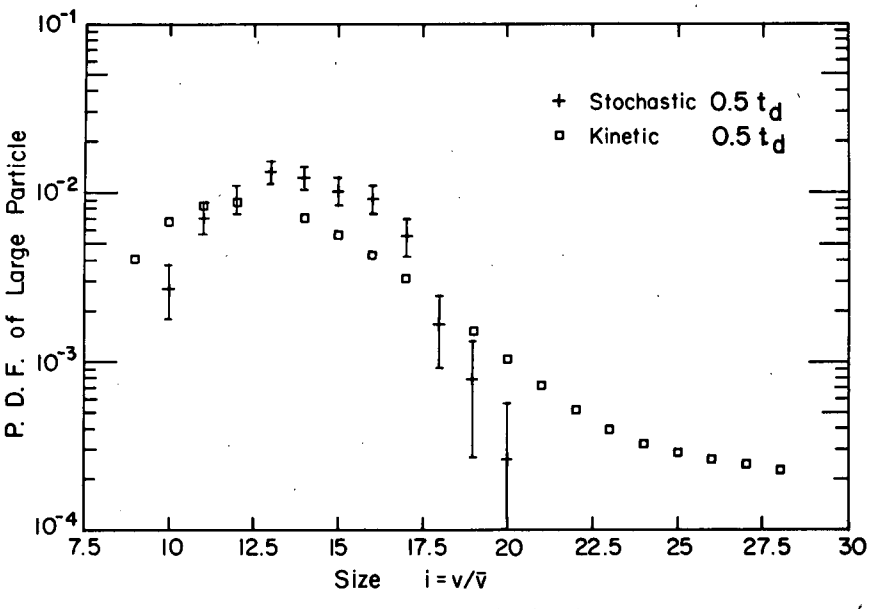

FIG. 11. As in Fig. 10 but for time $0.5t_d$.

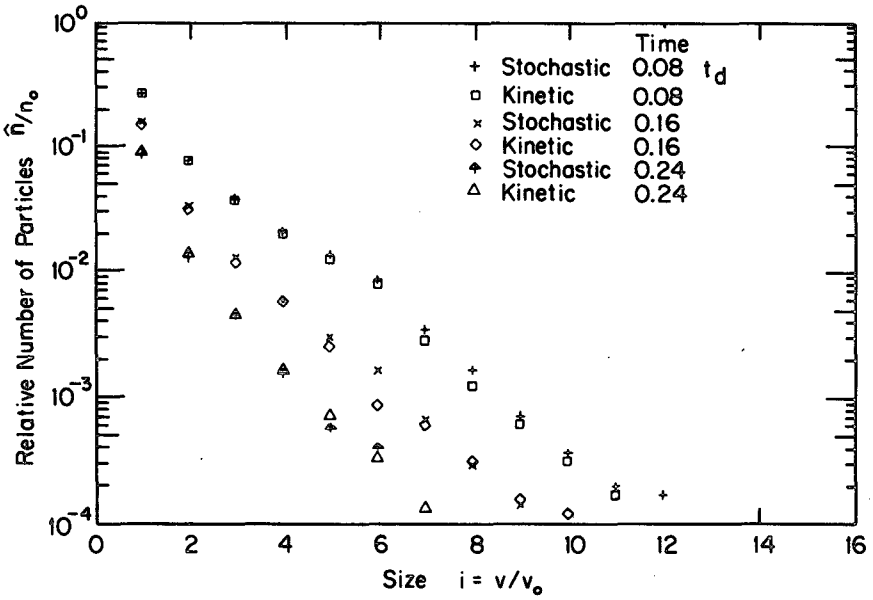

FIG. 12. Average particle size spectrum in differential sedimentation in the presence of particle removal by settling. Time scale $t_d = \mu/[n_0 r_0^4 g(\rho_p - \rho_f)]$, $t_d/t_f = 5$, $c_0 = 0.87\%$.

the nonlinearity in particle number of the coagulation process suggests that local fluctuations in the number concentration of the particles may give an average spectrum different from the one predicted by the kinetic coagulation equation.

In this paper, we tested the kinetic equation against the full stochastic coagulation equation, as formulated by Gillespie (1972, 1975b), using collision probabilities for particles corresponding to proposed physical collision mechanisms. More specifically, for Brownian diffusion, shear and differential sedimentation-induced coagulation, the results of our simulations suggest, for isolated volumes of fluid, that the kinetic equation, in general, produces an average size spectrum that

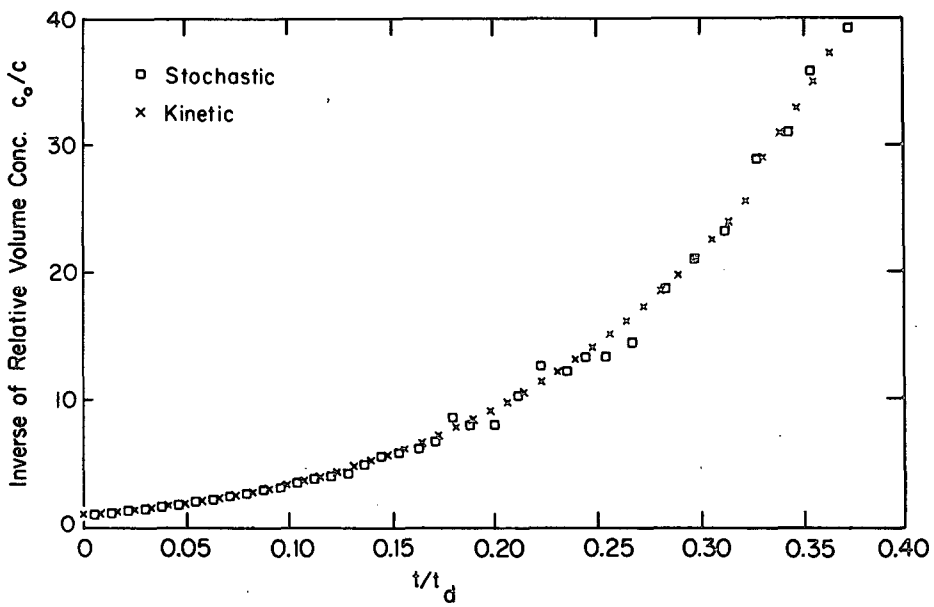

FIG. 13. Evolution of the particle volumetric concentration in differential sedimentation. Time scale $t_d = \mu/[n_0 r_0^4 g(\rho_p - \rho_f)]$, $t_d/t_f = 5$, $c_0 = 0.87\%$.

matches well the true stochastic average spectrum. However, the two models predict particle size distributions differing mainly in the large particle end of the spectrum where the occurrence of a particle is a rare event at times of the order of the characteristic time scale for the process or less. This is not insignificant when large particles may be particularly important to the further growth of the population, as, for example, in the production of rain in warm clouds.

The results obtained can be interpreted in a specific physical context to exemplify this result. To illustrate, consider a cloud volume of 100 cm^3 initially containing 10^5 droplets with radius 40 μm and diffusivity 3×10^{-8} cm^2 s^{-1} and in which the droplets experience a shear of magnitude[3] $G = 1$ s^{-1}. The characteristic times for coagulation are

$$t_b = (n_0 r_0 D_0)^{-1} = 3.3 \times 10^7 \text{ s};$$

$$t_s = (n_0 r_0^3 G)^{-1} = 10^6 \text{ s};$$

$$t_d = \mu[n_0 r_0^4 g(\rho_p - \rho_f)]^{-1} = 150 \text{ s}.$$

The characteristic time for settling depends on the vertical dimension h of the cloud. The normalized number distributions presented in Figs. 1–13 then, if multiplied by $n_0 = 10^3$ and the volume of the cloud (100 cm^3), will give the average number of particles of a given size remaining in the cloud volume at the time specified.

The characteristic times in the example above suggest that differential sedimentation-induced collisions are mainly responsible for rain formation by droplet coalescence in warm clouds. It is worth observing that the ratio $t_d/t_s = \mu G/[r_0 g(\rho_p - \rho_f)]$ decreases with increasing particle size so that the relative importance of differential sedimentation as a collision mechanism increases as larger particles are formed. The results of the simulations pertaining to differential sedimentation, when interpreted physically as discussed above, indicate that the differences between the kinetic and the stochastic approach become evident at times of the order of the appropriate time scale. If these times are shorter than the time scales for sufficient mixing between the droplet in the fluid volume under consideration with droplets in adjacent fluid, then the spatial inhomogeneities caused by the coagulation process will dominate. In the presence of settling then, the ratio of the characteristic time for coagulation to the characteristic time for settling is of importance. If the only spatial mixing mechanism is particle settling, then the magnitude of this time scale ratio is a significant indicator for the validity of the kinetic equation, since, for large values of this ratio, significant mixing is expected. It is interesting to observe that the kinetic model can be adequate for modeling the coagulation kinetics of a population of particles subjected to one collision mechanism, but may fail to model the same population of particles when subjected to a different collision mechanism. For example, a system of large particles with high excess density $\rho_p - \rho_f$ may be considered well-mixed for Brownian diffusion and shear-induced coagulation but poorly mixed for differential sedimentation-induced collisions.

The kinetic coagulation equation can be expressed in a normalized form, which specifies a *relative* number concentration of particles as a function of *relative* size and dimensionless time, and, in the case of settling, a dimensionless time scale ratio specifying the number of collisions during the settling process. Thus, there is no direct dependence on the absolute initial number concentration of particles. Solutions of the equation are therefore possible even when the absolute number is very small. The stochastic approach deduced by Gillespie (1972) avoids this problem and produces size distributions that truly reflect the actual particle statistics. Gillespie's (1972) analytically deduced arguments (see Section 1) regarding the conditions under which the kinetic equation is expected to be stochastically complete are in complete agreement with the results of the simulations performed in this study. The size distributions predicted by the kinetic model deviate more from the true stochastic average spectrum when the absolute number of particles per unit volume is small, since at large particle number concentrations correlations between particle properties tend to diminish. Furthermore, the discrepancies between the two models become apparent at a smaller number of particles in shear coagulation than in Brownian diffusion-induced coagulation. In the latter case, the collision function is proportional to $(j/i)^{1/3}$, where $j > i$, and i, j denote particle volume, while in shear it is proportional to (j/i). Thus, in Brownian diffusion, coalescence between particles of equal sizes is more important in determining the shape of the particle size distribution at later times. This observation is in accordance with Gillespie's assertion that correlations, whose strength affects the validity of the kinetic equation, are less important when the coalescence between particles of equal size is prohibited.

Finally, the simulations performed for the growth of a large particle sedimenting through a monodisperse population of smaller ones suggests that, for times approaching the characteristic time for coagulation, the stochastic model predicts a faster growth than the kinetic equation, as has been postulated by Warshaw (1967), Long (1971) and Twomey (1966). The opposite conclusion reached by Chin and Neiburger (1972), may be explained by their assumption of a constant number of small particles, since, in that

[3] This corresponds to a rate of turbulent kinetic energy dissipation per unit mass $\epsilon = 0.15$ cm^2 s^{-3} (see Saffman and Turner, 1956).

case, one of the factors creating particle correlations, namely the constraint of constant particle mass in a given volume of fluid, does not exist.

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